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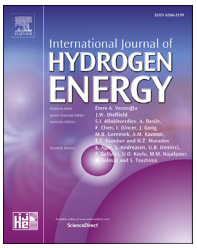

Synthesis of bifunctional non-noble monolithic catalyst Co-W-P/carbon cloth for sodium borohydride hydrolysis and reduction of 4-nitrophenol

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ABSTRACT

Amorphous Co-W-P catalysts, which were prepared on carbon cloth (CC) by electrodeposition, have been investigated as bifunctional non-noble catalysts for the hydrogen generation from alkaline $NaBH_4$ solution and the reduction of 4-nitrophenol by $NaBH_4$. Scanning electron microscopes (SEM), energy dispersive X-ray spectrometer (EDX), and X-ray diffraction (XRD) were used to characterize the Co-W-P/CC catalysts. The hydrogen generated catalytic properties of as-prepared catalysts with different content of P and the stability were investigated in the alkaline $NaBH_4$ solution of 5 wt% $NaBH_4$ and 2 wt% NaOH. The activation energy for hydrolysis of $NaBH_4$ by the Co-W-P catalyst was also probed at different temperature, and the results show that the obtained Co-W-P/CC catalysts exhibit very low apparent active energy (Ea = 27.18 kJ mol^{-1}). Finally, we detect the catalytic activity of Co-W-P/CC in the reduction of 4-nitrophenol for the first time, and it also presents outstanding catalytic capability with the apparent rate constant (k_{app}) of 11.91 × 10^{-3} s^{-1}. These characteristics indicate that the Co-W-P/CC catalysts possess a potential application on both the sodium borohydride hydrolysis and reduction of 4-nitrophenol.

Introduction

With the gradually decreased resources of fossil fuels and the rising challenges of environmental pollution, an urgent need is to develop a secure, clean and feasible new energy around the world. Hydrogen is an ideal replacement as an energy carrier for fuel cell applications, because it does not have any poisonous by-product to the environment, and does have a broad developing and applied prospect in the near future. Hydrogen possesses a high energy density of 120 kJ g^{-1}, which is three times more than that of petroleum, and it can be used

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in a fuel cell to power an engine at a high efficiency [1]. Sodium borohydride ($NaBH_4$) is one of the most widely studied chemical hydrides owing to its high hydrogen capacity (with a theoretical value of 10.8 wt%), easy control of the hydrogen generation rate (HGR), near-ambient operating conditions which are usually less than 60 °C (at 0.1 MPa hydrogen pressure), and the environmentally benign hydrolysis product ($NaBO_2$, sodium metaborate) *via* the following reaction equation: $NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2$ [2–7]. A variety of catalysts have been synthesized for catalytic hydrogen generation from $NaBH_4$ including loaded noble metal catalysts such as Ru [4,8], Pt [9,10], Rh [11] and Au [12]. Though noble metal catalysts exhibit high activity and stability, considering the expensive price of these noble metals, the researchers concentrate on the non-noble metals catalysts. Among those metals, cobalt-based catalysts get the most extensive research, for example, Co–B/open-CNTs [5], Ni–Co–P/g-Al_2O_3 [13], Co–P [14] and Co–Ni–B [15]. However, it is still a challenge to synthesize a high efficient catalyst.

It is well known that 4-nitrophenol (4-NP) is a common water pollutant and effluent in many drugs and dyes industries, while 4-aminophenol (4-AP) whose synthesis usually involves the reduction of 4-nitrophenol (4-NP) by sodium borohydride aqueous solution has extensive application as a photographic developer, anticorrosion lubricant, corrosion remover and is an important medical intermediate for the preparation of multifarious analgesic and antipyretic [16–20]. For the hydrogenation of 4-NP, non-noble metal catalysts have also been widely studied and applied, especially cobalt-based catalyst such as $Co_{0.85}Se$–Fe_3O_4 [21], FeCo [22], meso-Co-X (X = 150, 250, 350 and 450) [23]. Recently, Guo et al. [24] reported the catalytic property of Co-W-P catalysts supported on Cu substrates by electrodeposition. Wang et al. [25] prepared the Co-W-P catalyst which supported on γ-Al_2O_3. They both have in-depth exploration on hydrogen generation of $NaBH_4$ based on their catalysts. However, some significant parameters such as the effect of different content of P have not been investigated in their works. Further study is still urgent and necessary. Among the various supports, carbon cloth (CC) are often preferentially employed, which has the advantages of commercially available, flexibility, space-saving and high porosity [26,27]. Monolithic catalysts on the CC can be very convenient to recycle and reuse.

In this work, the non-noble monolithic catalyst Co-W-P/carbon cloth (CC) is synthesized by electrodeposition method. The hydrogen generated catalytic properties of as-prepared catalysts with different content of P and the stability are investigated in the alkaline $NaBH_4$, and the activation energy is also tested. In addition, we investigate the catalytic property for the reduction of 4-NP. Inspiringly, the Co-W-P/CC shows high hydrogenation behavior in the present of excess $NaBH_4$ at room temperature.

Experimental

Preparation and characterization of Co-W-P/CC

The Co-W-P catalysts were prepared on a piece of CC by electrodepositing method like our previous work [28]. Firstly, the CC was tailored into 1 cm^2 and weighed. Then the piece of CC was successively immersed into acetone, absolute ethyl alcohol and hydrochloric acid solution and ultrasonic washed for 10 min, 30 min and 5 min, respectively. After that, the piece of CC was dried in an oven and weighed again. Secondly, the electrolyte solution was prepared by pouring cobalt chloride ($CoCl_2 \cdot 6H_2O$), sodium hypophosphite ($NaH_2PO_2 \cdot H_2O$), sodium tungstate dehydrate ($NaWO_4 \cdot 2H_2O$) and orthoboric acid (H_3BO_3) into ethylene glycol solution ($(CH_2OH)_2$, 50% m^3/m^3) in sequence and the pH = 4 was adjusted by the addition of dilute sulphuric acid. After the electrodeposition for 20 min at 50 °C, the as-prepared catalyst was taken out, washed with distilled water for some times to remove residual impurity ions on the catalyst surface, and then dried in vacuum oven at 80 °C for 10 h. The ratio of those elements in the as-prepared is controlled by adjusting the proportion of reactants in the electrolyte solution. The appearance, chemical composition, and microstructure of the electrodeposited materials were characterized by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDX) and X-ray diffraction (XRD).

Catalytic hydrogen generation

The catalytic property of the as-prepared catalysts for hydrogen generation is evaluated by the water displacement method. The measurement system is illustrated in Fig. 1. Typically, a three-necked flask containing 10 ml 5 wt% $NaBH_4$ with 2 wt% NaOH is fitted with an outlet tube, which is connected to a homemade water-filled instrument for collecting evolved hydrogen gas. A piece of catalyst is put into the reaction flask with a thermostatic water bath to initiate hydrolysis reaction of $NaBH_4$ at 30 °C. As the reaction proceeding, the volume of water replaced by hydrogen is measured by homemade instrument calibration. The sample can be directly removed with forceps after reaction, and then washing it with deionized water for three times.

Catalytic reduction of 4-nitrophenol

The catalytic reduction of 4-NP is detected in a standard quartz cuvette with a path length of 1 cm at room temperature using $NaBH_4$ as hydrogen source. Fig. 2 shows the schematic

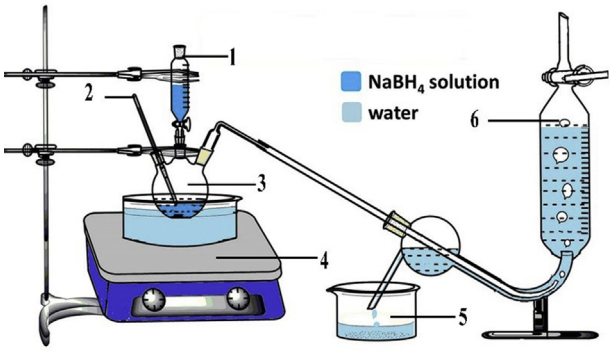

Fig. 1 – Experimental setup for hydrogen generation measurement.

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